

Formation and Growth of Hydride Blisters in Zr-2.5Nb Pressure Tubes

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Abstract

Hydride blisters were formed on the outer surface of Zr-2.5Nb pressure tube by a non-uniform steady thermal diffusion process. A thermal gradient was applied to the pressure tube with a heat bath kept at a temperature of 415°C and an aluminum cold finger cooled with flowing water of 15°C. Optical microscopy and three-dimensional laser profilometry were used to characterize the hydride blisters with different hydrogen concentrations and thermal diffusion time. Hydride blisters were expected to start at a hydrogen concentration of 30 - 70 ppm and a thermal diffusion time of 4 - 6×10^5 sec. The hydride blister size increases with higher hydrogen concentrations and longer thermal diffusion time. Some of the samples revealed cracks on the hydride blisters. The ratio of hydride blister depth to height was estimated as approximately 8:1.

Key Words : Hydride blister, CANDU pressure tube, Zr-2.5Nb alloy

1. Introduction

The hydride blister is one of the key issues to the safety of a CANDU reactor because it accompanies a volume expansion and sometimes cracking on the outer surface of the pressure tubes. The failure of a pressure tube in Pickering Unit 2 reactor in 1983 was caused by a contact between a pressure tube and calandria tube by the displacement of garter springs out of their original positions. The temperature gradient in the pressure tube wall caused the diffusion of

hydrogen and deuterium to the cold spot, initiating the formation of hydride blisters. A series of hydride blisters were found at the outer surface of pressure tube G-16. Some cracks in the hydride blisters grew by delayed hydride cracking (DHC). When the crack reached a critical size, a sudden through-wall fracture, 2 m long, developed in the axial direction [1].

Following the rupture, theoretical and experimental studies were carried out to understand the hydride blister formation of the pressure tubes [2-5]. Hydride blisters were grown

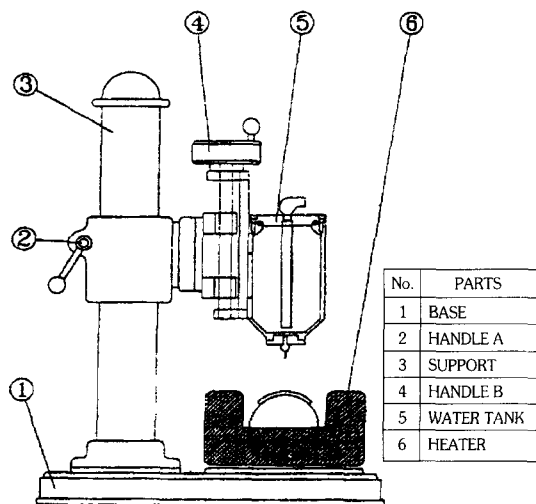


Fig. 1. Experimental Device for Blister Formation and Growth

No.	PARTS
1	BASE
2	HANDLE A
3	SUPPORT
4	HANDLE B
5	WATER TANK
6	HEATER

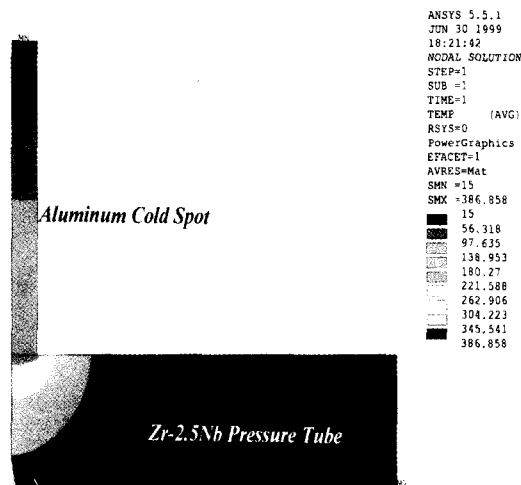


Fig. 2. Finite Element Calculation of the Temperature Field in the Specimen and Cold Finger

with a heat bath and a solid cold spot [6,7], and a liquid metal and air-jet cold spot [8]. A computer model of two-dimensional hydride blister growth shows that the growth rate in a two-phase zirconium/zirconium hydride region is insensitive to variation in the initial hydrogen concentration and in the subsequent hydrogen pick-up rate [5].

Although research results revealed many aspects of hydride blisters, details of hydride blister formation and cracking in the Zr-2.5Nb pressure tubes are not well understood. This paper attempted to find the critical conditions of formation of hydride blisters by reproducing hydride blisters in the laboratory. A wide range of hydride blister specimens with different thermal diffusion times and hydrogen concentrations were produced. The thermal gradient was applied by contact with an aluminum heat block on the inner surface and an aluminum cold finger on the outer surface. Hydride blisters were characterized by optical microscopy, three dimensional laser profilometry and x-ray diffraction. The initial stage of hydride blister formation and growth were analyzed with hydrogen concentrations and

thermal diffusion times. The significance of operating pressure tubes in contact with the calandria tubes is discussed with the critical depth of hydride blister.

2. Experiments

Curved rectangular specimens were cut out of Zr-2.5Nb pressure tube and charged with hydrogen by an electrolytic method in accordance with our procedures for characterization of Zr-2.5Nb pressure tubes [9]. Vacuum annealing was conducted to homogenize the hydrogen within the specimens at the temperatures above terminal solid solubility (TSS): $TSS = 1.2 \times 10^5 \exp(-Q/RT)$, where $Q = 8550$ cal/mole, $R = 1.987$ cal/mole, and $T =$ temperature K for Zr-2.5Nb alloy [10]. As a result, hydrides were found to uniformly distribute over the whole cross section of the specimen. Hydrogen concentration in the specimen was determined by chemical analysis after extracting small amount of specimen.

The hydride blisters were designed to nucleate and grow on the cold outer surface of the curved

specimen by applying thermal gradients across the thickness using the device, as shown in Fig. 1. The inner surface of the specimen sits on the aluminum block kept at $415 \pm 2^\circ\text{C}$, while the cold spot was made by keeping the outer surface in contact with the aluminum finger of 1 mm in diameter cooled by flowing water of $14 - 16^\circ\text{C}$. A finite element analysis was conducted to calculate the temperature gradient, as shown in Fig. 2, indicating that the temperatures of the outer surface in contact with the cold finger and the inner surface are 180°C and 370°C , respectively and a temperature gradient of around 190°C . This simulated result was confirmed with other experimental results [6]. This amount of temperature gradient is similar to one that the Zr-2.5Nb pressure tube contacted to the calandria tube has experienced in the reactor even though the hydrogen flux in this study is more accelerated than that in the real tube because of higher bulk temperature. In other words, this experiment is a kind of simulating experiment that accelerates the formation of the blisters.

The hydride blisters were formed after contact time of $1 - 6 \times 10^5$ seconds under the temperature gradient. The shape and dimension were determined by three-dimensional laser profilometry. The appearance and cross-sectional view of the hydride blisters were observed by optical microscope.

3. Results and Discussion

3.1. Critical Conditions of Hydride Blister Formation

Fig. 3 shows a typical view of the uniformly distributed hydrides after homogenizing treatment. The elongated hydrides in axial direction appeared mainly in the axial-circumferential plane of the pressure tube, suggesting that most hydrides

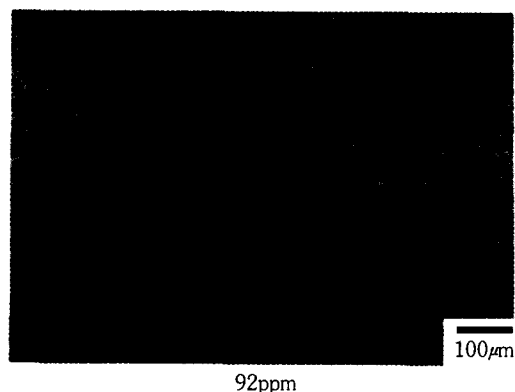


Fig. 3. Typical Hydride Distribution After Homogenization Annealing (Hydrogen concentration of 92 ppm)

preferentially precipitate on the grain boundaries of elongated α -Zr grains. Applying the temperature gradient of around 190°C between the region in contact with the cold finger and inner surface of the Zr-2.5Nb pressure tube induced the formation of hydride blisters.

Fig. 4 shows the evolution of a hydride blister with time and the hydrogen concentration under the constant temperature gradient. When the hydrogen concentration does not exceed 20 ppm, we can not clearly define the boundary of the hydride blister and the intact zirconium matrix, as shown in Figs. 4 (a) and (b). As the hydrogen concentration increases to 20 - 30 ppm, hydrides tend to agglomerate, but still revealing no definite blister boundary (Figs. 4 (c) and (d)). This observation can be correlated to the TSSP at the temperature of cold spot; the TSSP of the zirconium alloy [11] were be estimated as; 16 ppm at 150°C , 26 ppm at 180°C , 36 ppm at 200°C . When the hydrogen concentration increased to 36 - 75 ppm, however, the hydride blister began to form as shown in Figs. 4 (e) - (h), and grew to an ellipsoidal shape with some cracks inside (Fig. 4 (i)).

The net flux of hydrogen due to thermal diffusion is given by [4]

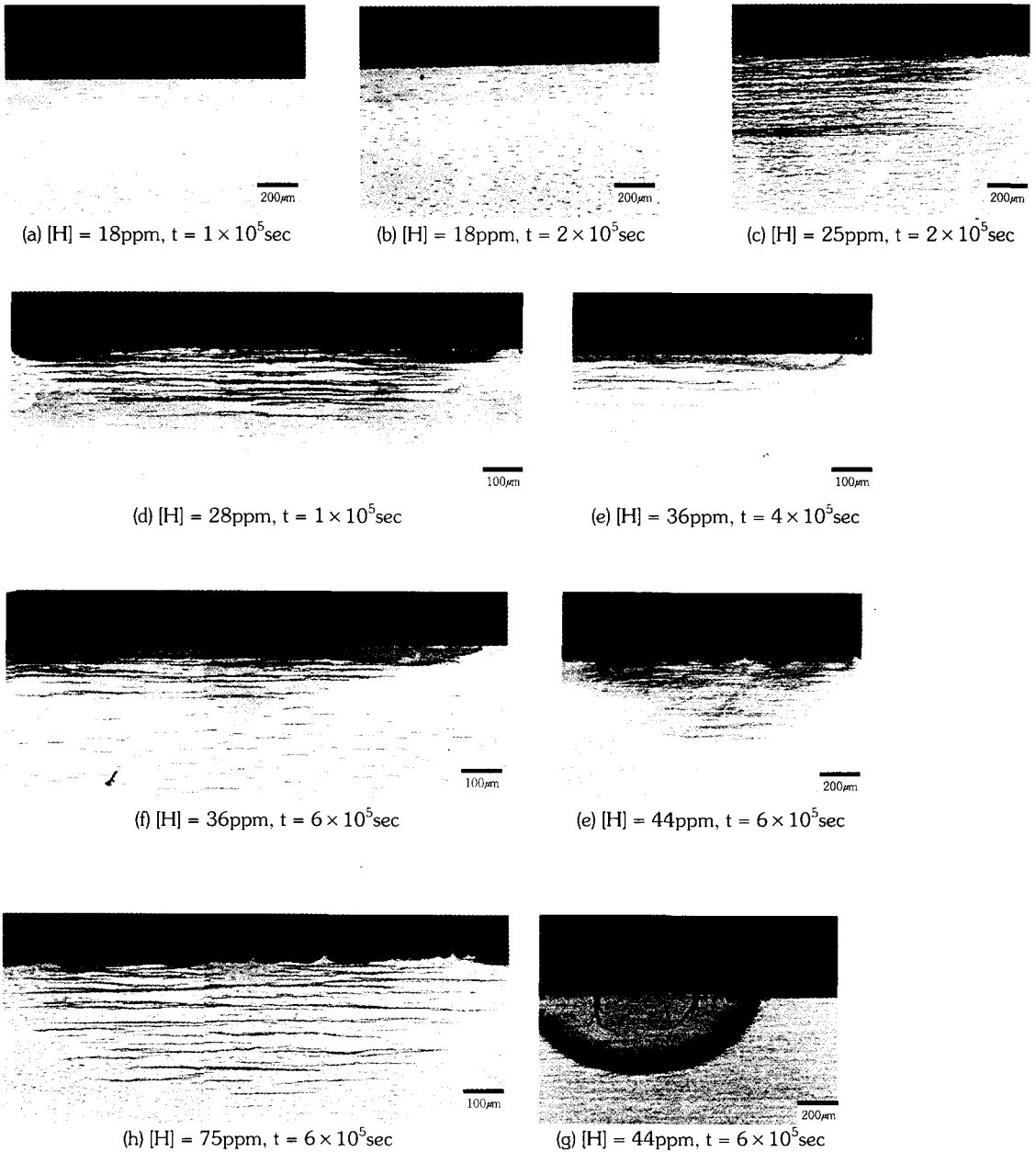


Fig. 4. Cross Sectional View of Hydride Blisters of Different Hydrogen Concentration and Thermal Diffusion Time

$$\bar{J} = -D\bar{\nabla}c - \frac{DQ^*}{RT^2}\nabla T \quad (1)$$

$$D = D_0e^{-Q/RT} \quad (2)$$

, where D is the diffusion coefficient for hydrogen in α -zirconium, R is the gas constant, T is the thermodynamic temperature at the cold spot, Q^* is the heat of transport, c is the hydrogen

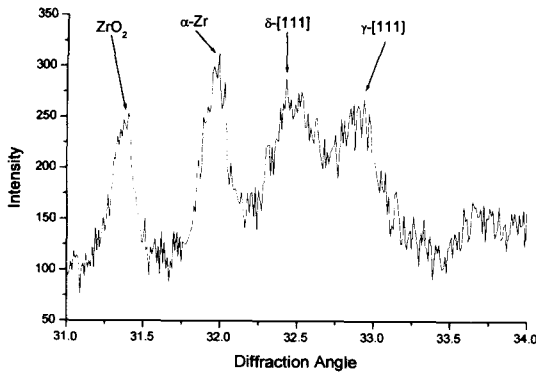


Fig. 5. Typical X-ray Diffraction Pattern of Hydride Blister

concentration, D_0 is frequency factor and Q is the activation energy for diffusion. The temperature gradient term, the second term of left side of the equation (1) is dominant for blister formation and growth and the experimental condition can be compared with actual temperature distribution in the pressure tube. We used higher T_{hot} (370°C) than actual pressure tube (310°C) and lower T_{cold} (180°C) than actual temperature at the contact (around 240°C). Assuming the effect of concentration gradient, the first term of left side of the equation (1), the net flux of hydrogen is estimated approximately three times higher than actual condition of pressure tube.

The phase composition of blister could vary from γ -hydride (fct structure with c/a ratio > 1.0 and a composition of approximately equivalent to ZrH), δ -hydride (fcc structure and a composition of $ZrH_{1.66}$), to ϵ -hydride (fct with c/a ratio < 1.0 and composition of ZrH_2) depending on the Zr-H composition. The δ -hydride is generally accepted stable phase in the hydride blister and the γ -hydride is a metastable phase formed at fast cooling [11]. A neutron diffraction study on the zirconium hydride exhibited both γ - and δ -hydride peaks at room temperature [12]. As shown in Fig. 5, our x-ray diffraction results of hydride blister indicated a two-phase mixture of γ - and δ -hydride

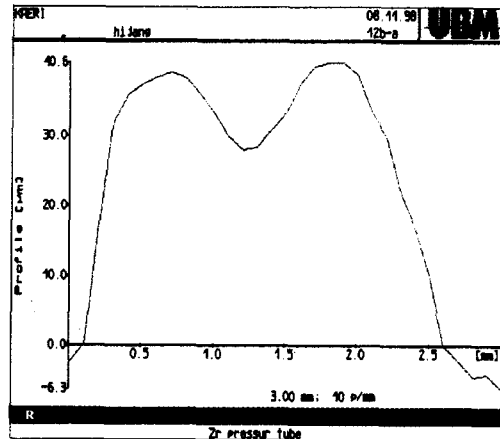
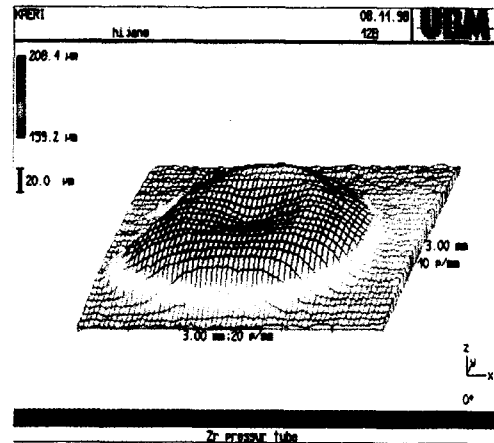


Fig. 6. Typical Output from Three Dimensional Laser Profilometry for a Hydride Blister

whose pattern is similar to that of the neutron diffraction.

The height and width of the hydride blisters were measured by three dimensional laser profilometry. A typical shape of hydride blister is shown in Fig. 6. The accuracy of the laser profilometry was $\pm 0.1\mu\text{m}$. It is evident that the blisters make the specimen swell, producing a non-negligible curvature of the surface, and thus modifying contact with the cold finger. A crater shaped profile was observed on several blisters probably due to an irregular contact between the cold finger and pressure tube and the inhibition of

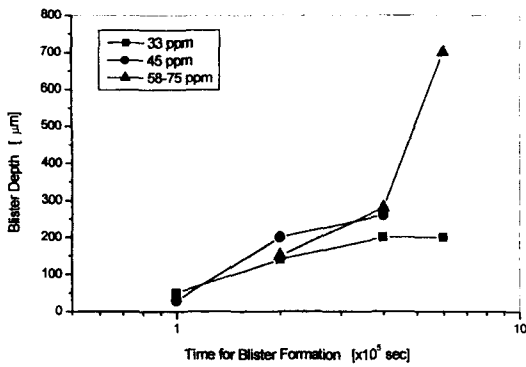


Fig. 7. Plot of Blister Depth vs. Time for Blister Formation

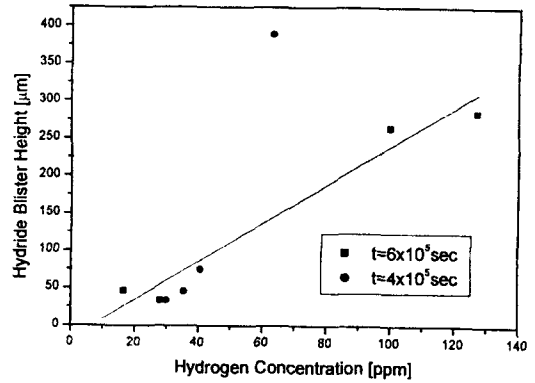


Fig. 9. Plot of Hydride Blister Height vs. Hydrogen Concentration

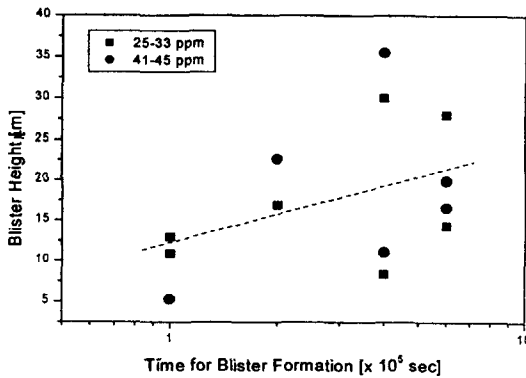


Fig. 8. Plot of Blister Height vs. Time for Blister Formation

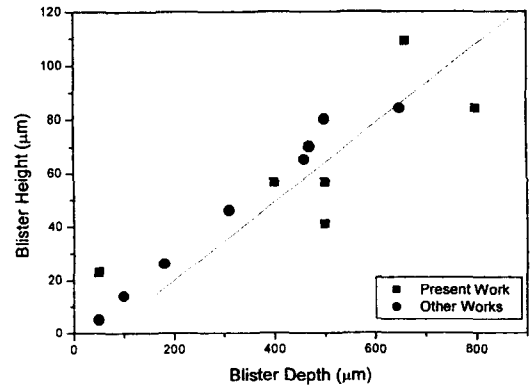


Fig. 10. Plot of Hydride Blister Height vs. Depth

swelling by pressing cold finger.

The blister height and depth were investigated with the contact time as shown in Figs. 7 and 8. It is obvious that the blister height or depth increased with increasing contact time in general. The blister depth ranged from 50 to 300 μm , while the blister height scattered mostly within the range of 10 to 40 μm . An abrupt increase in the blister depth occurred at the earlier contact time at the hydrogen concentration exceeding 45 ppm. However this trend was not clearly observed when the blister height was plotted as a function of the contact time. The blister height increased linearly

with the hydrogen concentration at the same contact time, as shown in Fig. 9.

Since the blister depth is one of the important parameter of the blistered pressure tube, it is necessary to characterize the blister depth. The equivalent depth of a blister is defined as the depth of pure δ -hydride, which has the same average weight fraction of hydrogen through the tube wall as the actual blister at the deepest point. If we establish the relationship between the blister depth and height, we may determine the blister depth without any destructive test only by measuring the blister height. Fig. 10 shows the relationship

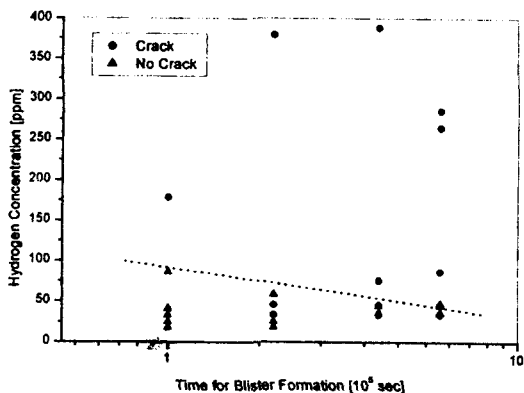


Fig. 11. Cracking Boundary in the Hydride Blisters, as a Function of Hydrogen Concentration and Thermal Diffusion Time

between the blister depth and height. The ratio of the blister depth to height was nicely fit to 8 to 1. This seems to be comparable to the ratios of 12 to 1 for blister formed by air jet [2] and of 10 to 1 for the blister formed by the contact of cooled round copper rods to the specimen surface [13]. The small difference in the ratio of the blister depth to height may come from a bit different test condition in association with the blister formation.

3.2. Cracking in Hydride Blister

Cracking in the grown blister may be very much susceptible to DHC. An attempt was made to define the boundary conditions in terms of the hydrogen concentration and time under which the cracks are not present inside the hydride blister. Fig. 11 shows the boundary conditions to define where the cracks are not present in the hydride blisters. When the hydrogen concentration exceeded 100 ppm, the cracks are always observed in the hydride blister. At the hydrogen concentration of 50 to 100 ppm, the possibility of the crack formation in the blister became higher with the increasing contact time. Especially, at low

concentration of less than 50 ppm, the cracks appeared in the blisters only after 4×10^5 seconds. These results indicate that the time to the formation of the cracked blister is much longer at lower hydrogen content than 50 ppm H.

The cracking of a hydride blister was also reported in the literature. Domizzi and et al. [6] observed cracks in their blister specimens, giving evidence of the fragile behavior of zirconium hydride (conditions of a hydrogen concentration of 300 ppm and a blister grown time of $1 \sim 6 \times 10^5$ sec). Leger and et al. [2] reported that many of the blisters formed either in the reactors or in the pressurized loop tests contained small cracks at the surface, whereas blisters grown with the air jets were not cracked as-grown.

An elastic finite element stress analysis of semi-ellipsoidal hydride blisters [14] showed that the expansion stress by the formation of blister decay to near zero at about one wall thickness away from a hydride blister and the highest stresses are developed under the blister at the deepest point. Relatively high compressive stresses ($-300 \sim -500$ MPa) could be developed on the center region of the hydride blister surface and slight tensile stresses ($0 \sim 100$ MPa) on the edge of the hydride blister surface. Therefore it is expected that the cracking might be inhibited, or at least initiated at the edge of the blister rather than center region of the blister surface. Since the finite element model assumed that the blisters are embedded in the tube wall rather than being surrounded by a spherical region and elliptical cross-section of hydride blisters, it may not exactly explain the cracking phenomenon in the hydride blister. Instead, cracking in our observation can be explained by the simple manner. The expansion stress due to the formation of hydride can be restricted to the direction of zirconium matrix, except to the direction of free blister surface, which results in a compressive stress state in the blister inside

region, while tensile stress in blister surface. Cracking on the blister surface can be appeared to release the tensile stress. However, it is not a simple task to describe such complex formation and growth of hydride blisters in non-isothermal zirconium alloys with a numerical analysis model.

3.3. Implementation to Wolsong Unit 1 Pressure Tubes

By extrapolating the data from Leemans and et al. [15], the critical depth of a hydride blister for a fracture is estimated as 420-620 μm at a design pressure of 160 MPa for Wolsong Unit 1. This means the blister grown under such a condition of contact time of 6×10^5 seconds (=6.9 days) and of hydrogen concentration exceeding 45 ppm (refer to Fig. 6) can be fractured at the design stress of Wolsong Unit. 1. In the operating Zr-2.5Nb pressure tube, the hydrogen pick-up rate is a really important factor to determine the time necessary to induce cracking of the blister. It is because the hydrogen pick-up rate determines the total hydrogen content dissolved in the tube. The deuterium concentration of the Zr-2.5Nb pressure tube in Wolsong Unit 1 was in the range of 5 - 20 ppm after 2947 effective full power days (EFPD) and the equivalent hydrogen uptake rate was in the range of 0.2 - 1.41 ppm/year [16]. By applying the concept of the equivalent depth for the blister to fracture, it would take 2,000 - 2,900 EFPD after the contact of the pressure tube with the calandria tube to form blister fracture at the hydrogen uptake rate of 1.3 ppm/year. In contrast, it would take a longer time such as 3,500 - 5,100 EFPD at the hydrogen uptake rate of 0.8 ppm/year. Because the inspection result showed at least more than 30% of the inspected tubes were in contact with the calandria tubes [17], the possibility of hydride blisters in Wolsong Unit 1 should be reviewed carefully. Furthermore, if the

hydrogen uptake rate increases gradually, the critical depth for the blister fracture could be reached within such a 10 years after the contact. It is worth of noting the importance of monitoring hydrogen uptake rate, non-destructive inspection of hydride blister, as well as remedial action such as SLAR (spacer location and repositioning).

4. Conclusions

1. Hydride blisters on the Zr-2.5Nb pressure tubes were successfully formed and grown using a device for a non-uniform steady temperature gradient of 190 °C. The hydrides tend to agglomerate at the hydrogen concentration of 20-30 ppm and an initial stage of blister formation was observed at a hydrogen concentration of 36-75 ppm and contact time of $4-6 \times 10^5$ seconds.
2. The profile height or depth of the blisters increased with a longer contact time for the specimens of hydrogen concentration of 36-75 ppm and the blister height increased linearly with increasing hydrogen concentration. The ratio of blister depth to the profile height was estimated as approximately 8:1, which is well comparable to the other work. Cracking in the blister appeared at the hydrogen concentration exceeding 100 ppm.
3. The blister depth grown under such a condition as the contact time of 6×10^5 seconds (=6.9 days) and hydrogen concentration exceeding 45 ppm reached the critical depth of a blister fracture at the design stress of an operating reactor. Because many of the inspected pressure tubes in the Wolsong Unit 1 were in contact with the calandria tubes and the critical depth for blister fracture is expected to reach within 10 operating years after the contact, it is worth of noting that hydrogen uptake rate should be monitored and nondestructive

examination of pressure tubes as well as remedial action such as SLAR should be performed periodically.

Acknowledgements

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